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(54) **Dye composition for Keratinous fibers.**

(57) A dye composition for keratinous fibers characterized by comprising the following ingredients (A), (B) and (C) :

(A) a direct dye,

(B) a polyoxyalkylene modified organopolysiloxane which contains 3 to 30% by weight of a polyoxyalkylene group in a molecule thereof, and is dispersible in water,

(C) an organic solvent,

and having a PH of 2.0 to 4.5.

The dye composition according to the present invention is excellent in the dyeing performance, and since it imparts excellent conditioning effects to the hair, the feel to the touch of the hair during rinsing and drying is quite favorable.

This invention relates to a dye composition for keratinous fibers for example human hair, and more particularly to a dye composition for keratinous fibers which is excellent in the dyeing ability and has excellent conditioning effects.

Conventional oxidation-type hair dye compositions are essentially composed of an oxidative dye and an oxidizer, and they involve danger of irritating the skin of the head or giving damages to the hair, if they are not handled properly with care, because hydrogen peroxide is reacted in the presence of an alkali in the course of the hair-dyeing operation. In order to overcome these problems which the oxidation-type hair dye compositions cannot avoid, semi-permanent dye compositions containing a direct dye are proposed as they give less adverse effects to the hair or the skin of the head.

The term "direct dye" throughout the description means the dyes which can express color without aid of other substances. In other words, it encompasses the dyes excepting oxidative dyes which first develop color when oxidized by an oxidizer such as hydrogen peroxide. Examples of the direct dye include nitro dyes, acidic dyes, basic dyes and disperse dyes.

However, these semi-permanent hair dye compositions in general are attended by a drawback. The feel of the hair i.e. its smoothness, softness and ease of finger combing at the time of rinsing and drying becomes worse because of the presence of a relatively great amount of a solvent. Finger combing is the running of the fingers through the hair. Good feel to the touch of the hair during rinsing through drying is important and is required especially for semi-permanent dye compositions which have recently been on the market because their manner of use is similar to that of hair rinses, in other words, applying a hair dye composition to the hair with bare hands or fingers and rinsing off subsequently. Enhanced hair conditioning effects are also demanded in this type of hair dye compositions.

In the meantime, there are many publications in this technical field. For instance, Japanese patent publication (kokoku) No. 55887/1986 discloses a method of providing conditioning effects with the dyed hair using a hair dye composition comprising a silicone derivative such as a polyether modified silicone; Japanese patent publication (kokai) No. 157713/1983 discloses a method of providing the hair with conditioning effects which last for a somewhat prolonged period by using a water-soluble cationic polymer and a water-soluble anionic surfactant; British patent No. 21753515 discloses a method of providing the hair with conditioning effects where a direct hair dye, cationic silicone surfactant and a hydroxyl silicone derivative are combined. Any of these methods does not fully meet consumers' needs in terms of conditioning effects during rinsing and drying.

In particular, it is to be noted that hair dye compositions containing an acid dye, which is a direct dye, are accompanied by a drawback of reduced hair-dyeing ability when quaternary salt type cationic surfactants which are widely used as a hair conditioning agent in hair care products. This is considered to be caused by water-insoluble complexes formed between the acid dye and the quaternary salt type cationic surfactant.

Accordingly, an object of this invention is to provide a dye composition for keratinous fibers comprising a direct dye, and is excellent in the dyeing ability and has excellent conditioning effects.

The above and other objects, features and advantages of this invention will become apparent from the following description.

The present invention is based on the finding that a combination use of a direct dye, a certain polyoxyalkylene modified organopolysiloxane and an organic solvent under a certain pH can provide a dye composition for keratinous fibers which is excellent in the feel to the touch of the hair during rinsing and drying.

According to the present invention, there is provided a dye composition for keratinous fibers characterized by comprising the following ingredients (A), (B) and (C):

(A) a direct dye,

(B) a polyoxyalkylene modified organopolysiloxane which contains 3 to 30% by weight of a polyoxyalkylene group in a molecule thereof, and is dispersible in water,

(C) an organic solvent,

and having a pH of 2.0 to 4.5.

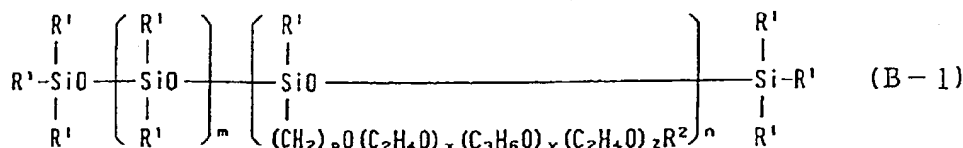
Examples of the direct dye (A) include nitro dyes such as 3-amino-4-hydroxynitrobenzene, 2-amino-5-hydroxynitrobenzene, 2-amino-3-hydroxynitrobenzene, 2-amino-5-N,N-bis-beta-hydroxyethylaminonitrobenzene, 2-amino-4-chloro-5-N-beta-hydroxyethylaminonitrobenzene, 2-amino-4-methyl-5-N-beta-hydroxyethylaminonitrobenzene, 3,4-bis-(N-beta-hydroxyethylamino)nitrobenzene, 2-amino-4-methyl-5-N-beta, gamma-dihydroxypropylaminonitrobenzene, 2-amino-4-methyl-5-beta-aminoethylaminonitrobenzene, 2-amino-4-hydroxynitrobenzene, and in particular 3,4-diaminonitrobenzene, 2,5-diaminonitrobenzene, 2-amino-5-N-beta-hydroxyethylaminonitrobenzene, 2-N-beta-hydroxyethylamino-5-N,N-bis-beta-hydroxyethylaminonitrobenzene, 2-N-methylamino-5-N,N-bis(beta-hydroxyethyl)aminonitrobenzene, 2-N-methylamino-5-N-methyl-N-beta-hydroxyethylaminonitrobenzene, 2-N-beta-hydroxyethylamino-5-hydroxynitrobenzene, 3-methoxy-4-N-beta-hydroxyethylaminonitrobenzene, 4-nitro-3-methylaminophenoxy ethanol, 2-N-beta-hydroxyethylamino-5-amino nitrobenzene, 2-N-beta-hydroxyethylaminonitrobenzene, 3-amino-4-N-beta-hydroxyethylaminonitro-

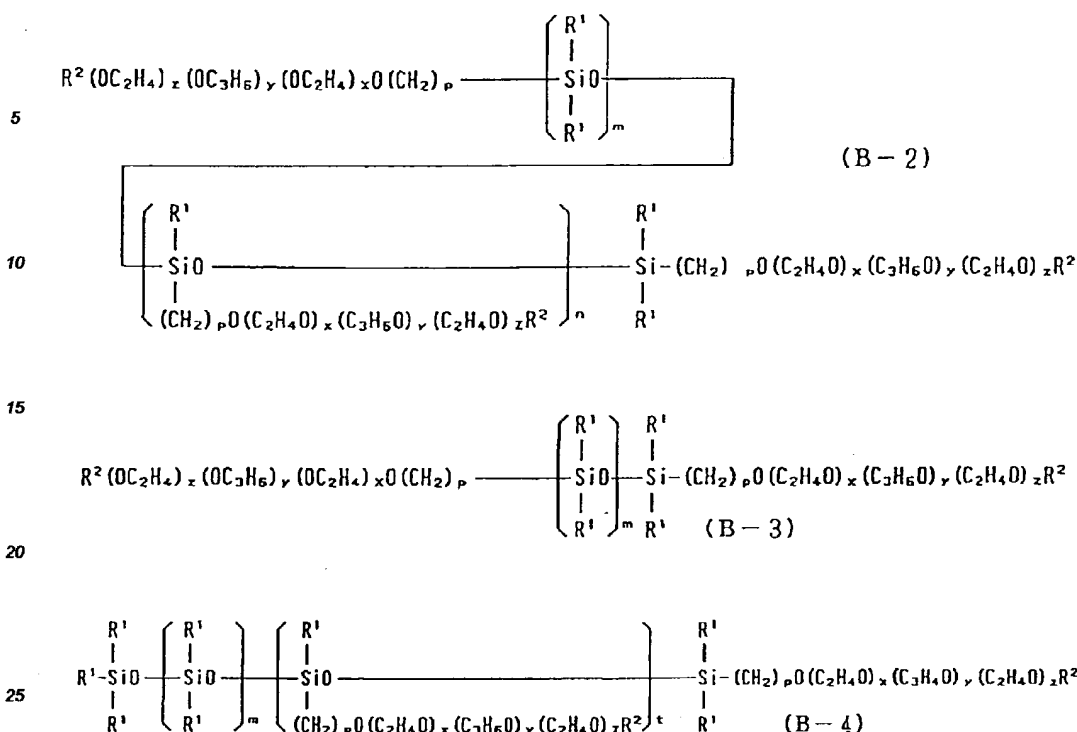
benzene, 3-beta-hydroxyethoxy-4-N-beta-hydroxyethylaminonitrobenzene, 2-amino-5-N-methylaminonitrobenzene, 2-amino-3-methylnitrobenzene, 2-N-beta-hydroxyethylamino-5-beta, gamma-dihydroxypropyloxynitrobenzene, 3-hydroxy-4-N-beta-hydroxyethylaminonitrobenzene, 3-hydroxy-4-aminonitrobenzene, 2,5-N,N'-beta-hydroxyethylaminonitrobenzene, 2-N-methylamino-4-o-beta, gamma-dihydroxypropyloxynitrobenzene, 2-N-beta-aminoethylamino-5,N,N-bis-(beta-hydroxyethyl)aminonitrobenzene, 2-N-beta-aminoethylamino-4-methoxynitrobenzene, 1-amino-4-methylaminoanthraquinone, 1,4-diaminoanthraquinone; acid dyes such as C.I. Acid Red 27, C.I. Acid Red 51, C.I. Acid Red 18, C.I. Acid Red 92, C.I. Acid Red 94, C.I. Acid Red 52, C.I. Acid Yellow 23, C.I. Food Yellow 3, C.I. Food Green 3, C.I. Food Blue 2, C.I. Acid Blue 74, C.I. Pigment Red 57-1, C.I. Acid Red 33, C.I. Acid Red 87, C.I. Acid Red 92, C.I. Acid Red 94, C.I. Acid Orange 7, C.I. Acid Red 95, C.I. Acid Yellow 73, C.I. Acid Yellow 3, C.I. Acid Green 25, C.I. Solvent Green 7, C.I. Acid Green 5, C.I. Acid Blue 5, C.I. Acid Blue 9, C.I. Acid Orange 24, C.I. Acid Violet 9, C.I. Food Red 6, C.I. Acid Red 26, C.I. Food Red 1, C.I. Acid Red 88, C.I. Acid Orange 20, C.I. Acid Yellow 40, C.I. Acid Yellow 1, C.I. Acid Yellow 36, C.I. Acid Yellow 11, C.I. Acid Green 1, C.I. Acid Green 3, C.I. Acid Violet 43 and C.I. Acid Black 1; oil-soluble dyes such as C.I. Solvent Red 49, C.I. Solvent Red 48, C.I. Solvent Red 43, C.I. Solvent Red 72, C.I. Solvent Red 73, C.I. Acid Yellow 73, C.I. Solvent Yellow 33, C.I. Solvent Green 3, C.I. Solvent Violet 13, C.I. Solvent Red 24, C.I. Solvent Orange 7, C.I. Solvent Orange 2, C.I. Solvent Yellow 5, C.I. Solvent Yellow 6 and C.I. Solvent Blue 63; disperse dyes such as C.I. Solvent Red 49, C.I. Solvent Red 48, C.I. Solvent Red 43, C.I. Solvent red 23, C.I. Solvent Red 72, C.I. Solvent Red 73, C.I. Acid Yellow 73, C.I. Solvent Yellow 33, C.I. Solvent Green 3, C.I. Solvent Violet 13, C.I. Solvent Red 24, C.I. Solvent Orange 7, C.I. Solvent Yellow 5, C.I. Solvent Yellow 6 and C.I. Solvent Blue 63; basic dyes such as C.I. base violet and C.I. Solvent Red 49; basic dyes manufactured by Williams Co., such as Sienna Brown, Mahogany, Madder Red, Steel Blue and Straw Yellow; disperse dyes such as Disperse Black 9, Disperse Blue 1, Disperse Blue 3, Disperse Violet 1 and Disperse Violet 4.

For preparing dye compositions according to this invention in a so-called rinse type which can be used by bare hands or fingers, the following direct acid dyes are preferred: C.I. Acid Yellow 23, C.I. Solvent Green 7, C.I. Acid Red 27, C.I. Acid Red 18, C.I. Food Green 3, C.I. Food Blue 2, C.I. Acid Blue 9, C.I. Acid Yellow 1, C.I. Acid Red 52, C.I. Pigment Red 57-1, C.I. Acid Orange 7, C.I. Acid Black 1, C.I. Acid Green 25, C.I. Acid Violet 43, in particular, C.I. Acid Black 1, C.I. Acid Violet 43, C.I. Acid Orange 7, C.I. Acid Yellow 1 and C.I. Acid red 52.

These direct dyes are employed singly or as a mixture of two or more. They are incorporated into the dye compositions according to the present invention in an amount of 0.02 to 5% by weight (hereinafter may be referred to %), and more preferably 0.02 to 1% based on the total amount of the dye composition. An amount less than 0.01% cannot achieve a sufficient dyeing effect, and amount exceeding 5% will cause significant staining of the skin of hands and fingers, thus not practical. In the case where the dye compositions of this invention are formed into rinse-type compositions which can be handled by bare hands or fingers, the amount of the dyes is preferably 0.02 to 0.1% in view of the balance between the dyeing performance and ignorable staining to the skin.

Ingredient (B) is a polyoxyalkylene modified organo-polysiloxane which contains 3 to 30% by weight of a polyoxyalkylene group in a molecule thereof and is dispersible in water as mentioned before. Polyoxyalkylene groups may be present at any position of the polysiloxane chain, and the following structures (B-1) to (B-4) may be mentioned.





wherein R<sup>1</sup> is a C1 to C3 alkyl or phenyl group, R<sup>2</sup> is a hydrogen atom or a C1 to C12 alkyl group, m is an integer of 20 to 200, n is an integer of 1 to 10, x is an integer of 0 to 15, y is an integer of 0 to 15, z is an integer of 0 to 15, p is an integer of 1 to 5, t is an integer of 0 to 10, provided the sum of x+y+z is 1 or more but 20 or less.

The proportion by weight of the polyoxyalkylene group contained in a molecule of the polyoxyalkylene modified organopolysiloxane (B) is preferably from 3 to 30%, and more preferably 5 to 25%. A proportion less than 3% cannot achieve excellent conditioning effects because the polyoxyalkylene modified organopolysiloxane will become difficult to disperse in water. Further, users will feel friction at the time of rinsing the hair. On the other hand, proportion exceeding 30% will make the modified polysiloxane easy to dissolve in water such as rinse water, which eventually provides reduced conditioning effects because it is readily rinsed off with water.

The polyoxyalkylene modified organopolysiloxanes which are useful in the present invention is capable of being dispersed in water of 25°C, providing no or very much reduced frictional feel to the touch of the hair at the time of rinsing while imparting excellent conditioning effects at the time of drying the hair, that is, no or very much reduced frictional feel to the touch of the hair and proper and agreeable smoothness and softness.

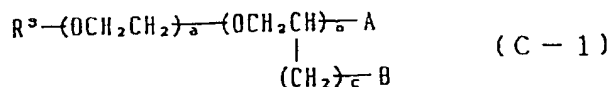
Here, the polyoxyalkylene modified organopolysiloxanes which are capable of being dispersed in water according to this invention are such that an aqueous 1% solution of the modified organopolysiloxanes cannot transparently dissolve and observed as turbid by the naked eye. Part of the modified organopolysiloxanes may float on the surface or settle, which is also within the scope of this invention.

These polyoxyalkylene modified organopolysiloxanes are employed singly or as a mixture of two or more. The amount of the modified organopolysiloxanes are preferably 0.01 to 10%, more preferably from 0.1 to 4% based on the total amount of the dye composition of this invention. An amount less than 0.01% cannot achieve a sufficient hair conditioning effect, while an amount exceeding 10% will make the composition sticky thus not favorable.

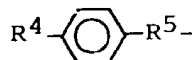
The dye compositions according to the present invention can be formed into ordinary forms of conventional hair dye compositions. That is, a hair dye composition is applied onto keratinous fibers such as the hair by using gloves, etc., allowed to stand for a certain period of time and subsequently rinsed off. Another form of the dye compositions of this invention, which is more preferable, is that of a hair rinse-type. In this case, a composition is directly applied to the hair or the like with bare hands or fingers, allowed to stand for a short time of from 30 to 300 seconds, and subsequently rinsed off. In the latter case, the dyeing effects are visually

acknowledged upon repeated use of 5 to 10 times in general, which might be varied depending on the type of the hair fiber and manner of use.

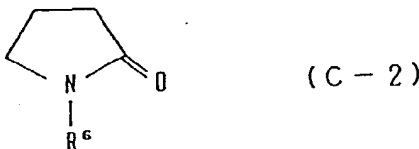
The organic solvents (C) which are useful in this invention include the compounds represented by formula (C-1) below, C1 to C4 alkylene carbonates, and N-alkylpyrrolidones represented by formula (C-2):



wherein  $R^3$  is a hydrogen atom, a lower alkyl group or a group



wherein  $R^4$  is a hydrogen atom, methyl group or a methoxy group,  $R^5$  is a hand for bonding or a C1 - C3 saturated or unsaturated divalent hydrocarbon, A and B independently represent a hydrogen atom or a hydroxyl group, a, b and c independently represent an integer of 0 to 5, excepting the two cases where  $a=b=c=0$  and  $A=H$ , and  $a=b=c=0$ ,  $R^3=H$  and  $A=OH$ ;



wherein  $R^6$  is a C1 - C18 linear or branched alkyl group.

Examples of the organic solvents according to the present invention include ethanol, isopropanol, n-propanol, n-butanol, isobutanol, ethylene glycol, propylene glycol, isoprene glycol, 1,3-butanediol, benzyl alcohol, cinnamic alcohol, phenethyl alcohol, p-anisyl alcohol, p-methylbenzyl-alcohol, phenoxyethanol, 2-benzyloxy ethanol, methyl carbitol, ethyl carbitol, propyl carbitol, butyl carbitol, triethylene glycol monoethylether, triethylene glycol monobutyl ether, glycerol, N-methylpyrrolidone, N-octylpyrrolidone, N-laurylpyrrolidone and the like. It is preferred that these organic solvents (C) be incorporated into the dye composition of this invention in an amount of from 0.5 to 50%, preferably 1 to 35% based on the total weight of the composition. An amount less than 0.5% cannot achieve a sufficient dyeing performance in a short time of contact of the composition with the hair in case where a "rinse-type" dye composition to be handled with bare hands or fingers is prepared. An amount exceeding 50% is not advisable either, because improvements of the effects will no more be expected.

The pH of the dye compositions according to the present invention as measured on an aqueous 10% solution of the composition is preferably from 2.0 to 4.5, more preferably from 2.5 to 4.5 and most preferably from 2.5 to 4.0. When the compositions are formed into a rinse type, where bare hands or fingers come into direct contact with the compositions, a pH exceeding 4.5 is not advisable because the time during which the compositions are in contact with the hair cannot be shortened, while on the other hand, a pH lower than 2.0 raises a problem of irritating the skin due to its acidity.

It is preferred that the compositions according to this invention be so formulated that the buffer index of an aqueous 10% solution of the compositions is from 0.01 to 0.2 gram equivalent/litre, in view of the reduced contact time after application of the compositions to the hair. Here the buffer index is a value calculated from the following equation, factoring the concentration of the base required for elevating the pH of an aqueous 10% solution of the dye composition at 25°C by value 1 from the initial value.

$$\text{Buffer Index} = \left| \frac{dC_B}{dpH} \right|$$

wherein  $C_B$  is an ion concentration of a base (gram equivalent/litre).

A buffer index less than 0.01 gram equivalent/litre cannot achieve a sufficient dyeing effect in a short time of contact, whereas an index value exceeding 0.2 gram equivalent/litre cannot improve the dyeing effect remarkably. Also, the pH buffering agent or other ingredients to be incorporated are difficult to dissolve in the composition, thus not preferable. Preferable range of the buffer index, therefore, is 0.01 to 0.05 gram equivalent/litre.

The buffer capability according to the invention can be given to the composition by adding thereto pH buffer agents, surfactants, chelating agents, preservatives and the like. Among them, pH buffering agents are those showing the buffer action in a pH range of pH 2.0 to 4.5 and selected from organic acids, inorganic acids and/or their salts. Examples of the organic acids include citric acid, glycolic acid, succinic acid, tartaric acid, lactic acid, fumaric acid, malic acid, levulinic acid, butyric acid, valeric acid, oxalic acid, maleic acid and mandelic acid. Examples of the inorganic acids include phosphoric acid, sulfuric acid and nitric acid. Examples of the salts of these acids include sodium salts, potassium salts, ammonium salts and alkanolamine salts such as triethanolamine salts. The amount of the buffer compounds to be incorporated is not particularly limited and depends on the compounds used. For instance, when a sodium salt of citric acid is used as a buffer compound, the concentration of the salt is higher than about 2 - 2.5 wt %.

The hair dye compositions according to this invention may contain optional ingredients such as surfactants; cationic polymers; oils; viscosity modifiers such as hydroxyethylcellulose and xanthane gum; silicone derivatives other than the mentioned ingredients (B); perfumes; preservatives; UV absorbers; antioxidants; bactericides; pearlescent agents; opacity agents and the like as long as they will not impede the effects of the present invention. Here, examples of surfactants include anionic surfactants such as olefin sulfonic acid, alkane sulfonic acid, aliphatic alkyl ether carboxylic acid and N-acylamino acid; amphoteric surfactants such as amidobetaine, carbobetaine and hydroxysulfobetaine; cationic surfactants such as mono- or di- alkyl quaternary ammonium salts; and nonionic surfactants such as polyoxy-alkylene alkyl ethers. Examples of cationic polymers include cationized cellulose, cationized starch, cationized guar gum, polymers of diallyl quaternary ammonium salts, copolymers of diallyl quaternary ammonium salt/acrylic amide and copolymers of hydroxyethylcellulose/dimethyl diallyl quaternary ammonium salt. Examples of oils include aliphatic esters, linear or branched alkyl glyceryl ethers and branched higher alcohols.

The dye compositions for keratinous fibers according to the present invention are prepared by any known processes, by blending the aforementioned ingredients. The manner of use of the compositions is described hereinbefore.

The dye compositions of this invention are excellent in the dyeing performance and in the conditioning effects providing very much favorable feel to the touch of the hair at the time of rinsing and drying the hair.

#### Examples

The present invention will now be described in more detail by way of examples, but they should not be construed as limiting the invention thereto.

#### Examples 1 to 3:

About 10 g of dry white hair fibers were shampooed, drained, and uniformly and quickly applied with 3 g of a composition in Table 1, allowed to stand for 30 seconds at 35°C, followed by rinsing and drying. A panel consisting of 10 expert members evaluated each composition with respect to the following items during rinsing and drying the hair. The results are shown in Table 1.

##### Evaluations on conditioning effects:

##### a) Finger Combing during Rinsing:

- A: No frictional feel with excellent smooth finger combing
- B: Reduced degree of frictional feel with moderate finger combing
- C: Certain degree of frictional feel with unfavorable finger combing
- D: Very frictional feel with catching

##### b) Softness of the hair during rinsing and drying:

- A: Very soft and resilient
- B: Soft
- C: Lack of softness

##### c) Combing at the time of drying the hair:

- A: Easy combing and smooth
- B: A little catching when combing
- C: Catching especially at the end of hair fibers

Table 1

(% by weight)

		Compara. Compn.			Invention Compn.		
		1	2	3	1	2	3
5	(1) Ethanol (%)	25.0	25.0	25.0	25.0	25.0	25.0
10	(2) Benzyl alcohol (%)	5.0	5.0	5.0	5.0	5.0	5.0
	(3) Citric acid (%)	0.5	0.5	0.5	0.5	-	3.0
15	(4) C.I. Acid Black 1 (%)	-	-	-	-	0.03	-
	(5) C.I. Acid Violet 43 (%)	-	-	-	-	0.03	-
20	(6) C.I. Acid Orange 7 (%)	0.05	0.05	0.05	0.05	-	0.05
	(7) Polyoxyethylene-modified organopolysiloxane (See note 1)	-	-	-	1.0	1.0	2.5
25	(8) Polyoxyethylene-modified organopolysiloxane (See note 2)	-	-	1.0	-	-	-
30	(9) Cationized Cellulose (See note 3)	0.5	-	-	-	-	-
	(10) Hydroxyethyl-cellulose	1.5	1.5	1.5	1.5	1.5	1.5
	(11) NaOH	← Suitable Amount (See note 4) →					
35	(12) Water	← Balance →					
	Finger combing during rinsing	C	D	C	B	B	A
40	Softness of the hair during rinsing and drying	B	C	C	A	A	A
45	Combing at the time of drying the hair	C	C	B	A	A	A

note 1) Polyoxyethylene group: 20 wt.%; MW: about 7500; Formula (B-1) where  $R^1=CH_3$ ,  $R^2=H$ ,  $M=70$  to  $80$ ,  $n=2$  to  $4$ ,  $x=10$  to  $12$ ,  $y=z=0$ ,  $p=3$ .

note 2) Polyoxyethylene group: 50 wt.%; Formula (B-1) where  $R^1=CH_3$ ,  $R^2=H$ .

note 3) Polymer JR400 manufactured by UCC Co.

note 4) Amount required for adjusting the pH to 4.0.

## Example 4:

Ten female monitors in their forties used the invention composition 3 (see Table 1) in the following manner. About 10% of their front hair was white. Beauticians shampooed the monitors' hair and applied about 15 g of the composition. The composition was allowed to stand for 60 seconds at 35°C, rinsed and dried with a hair drier. This cycle of operation was repeated for four times, and conspicuousness of white hair was visually evaluated by a panel consisting of ten members. The results are shown in Table 2.

Table 2

	No change in conspicuousness of white hair	Conspicuousness of white hair is somewhat mitigated	White hair is no more conspicuous
Invention composition 3	13	65	22

Note) The change in the color of the hair of the monitors before and after the use of the composition was observed by panel members, and classified into 3 groups of "No change in conspicuousness of white hair", "Conspicuousness of white hair is somewhat mitigated" and "White hairs are no more conspicuous". Ten panel members evaluated the results of 10 monitors, accordingly, the total number of data is 100.

## Example 5:

A composition having the following formulation was prepared. The composition was applied to a sample of Caucasian blond hair (2.5 g/5 g of hair) and allowed to stand for 30 minutes at 30°C, followed by rinsing with running water and drying. The feel to the touch of the hair during rinsing and drying was very good.



(Formulation)		
(1)	C.I. Steel Blue	0.025 (%)
(2)	2-Amino-5-beta-N-hydroxyethylaminonitrobenzene	0.050
(3)	Trimethyl ammonium behenyl chloride	1.0
(4)	Cetostearyl alcohol	4.0
(5)	Propylene glycol	7.0
(6)	Polyoxyethylene modified organopolysiloxane (Polyoxyethylene group: 20 wt.%; MW: about 5500; Formula B-1 where $R^1=CH_3$ , $R^2=H$ , $m=50-55$ , $n=2-3$ , $x=9-11$ , $y=z=0$ , $p=3$ )	2.0
	NaOH	Suitable Amount (Adjusted to pH 4.3)
(8)	Phosphoric acid	Suitable Amount (Adjusted to pH 4.3)
(9)	Water	Balance

## Example 6:

The similar procedures were followed as described in Example 5 using the following composition. The feel to the touch of the hair during rinsing and drying was very good.

(Formulation)		
(1)	1,3-Butylene glycol	20.0 (%)
(2)	2-Benzyloxyethanol	7.0
(3)	Lactic Acid	2.0
(4)	C.I. Acid Black 1	0.02
(5)	C.I. Acid violet 43	0.02
(6)	C.I. Acid Orange 7	0.04
(7)	Polyoxyethylene modified organopolysiloxane (Polyoxyethylene group: 18 wt.%; MW: about 6700; Formula B-2 where $R^1=CH_3$ , $R^2=H$ , $m=65-75$ , $n=1$ , $x=8-10$ , $y=z=0$ , $p=3$ )	1.5
(8)	Hydroxyethylcellulose	1.5
(9)	NaOH	Suitable Amount (Adjusted to pH 3.5)

## Example 7:

The similar procedures were followed as described in Example 5 using the following composition. The feel to the touch of the hair during rinsing and drying was very good.

5	(Formulation)	
	(1) Ethanol	20.0 (%)
10	(2) Benzyl alcohol	7.0
	(3) Lactic Acid	2.0
	(4) C.I. Acid Black 1	0.01
15	(5) C.I. Acid Violet 43	0.01
	(6) C.I. Acid Red 33	0.03
20	(7) Polyoxyethylene modified organopolysiloxane (Polyoxyethylen group: 7 wt.%; MW: about 13000; Formula B-3, where $R^1=CH_3$ , $R^2=H$ , $m=150-170$ , $x=8-12$ , $y=z=0$ , $p=3$ )	2.5
	(8) Xanthan gum	1.0
25	(9) NaOH	Suitable Amount (Adjusted to pH 3.0)

## Example 8:

The similar procedures were followed as described in Example 5 using the following composition. The feel to the touch of the hair during rinsing and drying was very good.

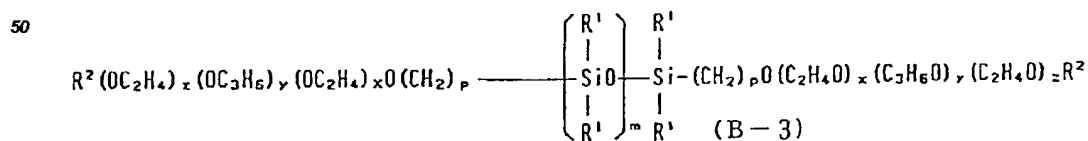
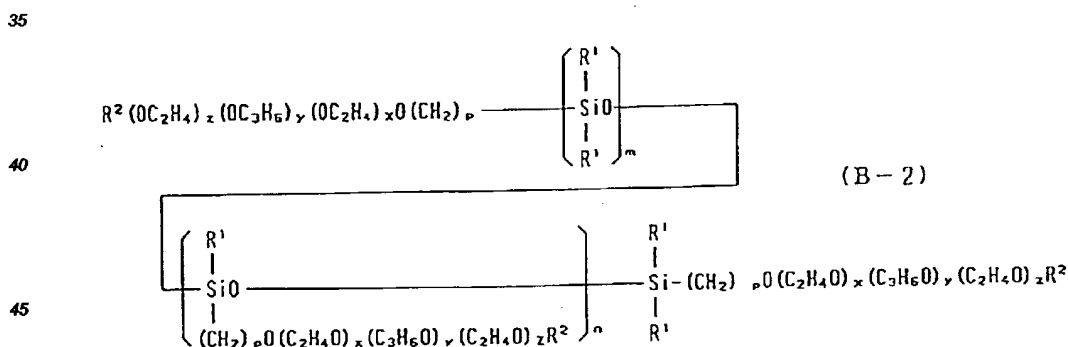
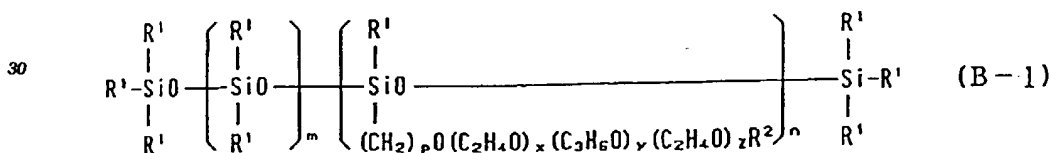
30	(Formulation)	
	(1) Ethanol	20.0 (%)
35	(2) Benzyl alcohol	3.0
	(3) Citric acid	2.0
	(4) C.I. Acid Black 1	0.01
40	(5) C.I. Acid Violet 43	0.01
	(6) C.I. Acid Red 33	0.03
45	(7) Polyoxyethylene modified organopolysiloxane (Polyoxyethylene group: 19 wt.%; MW: about 4200; Formula B-1, where $R^1=CH_3$ , $R^2=H$ , $m=35-45$ , $n=1-3$ , $x=8-10$ , $y=z=0$ , $p=3$ )	0.5
	(8) Hydroxyethylcellulose	1.5
50	(9) NaOH	Suitable Amount (Adjusted to pH 4.0)

## Claims

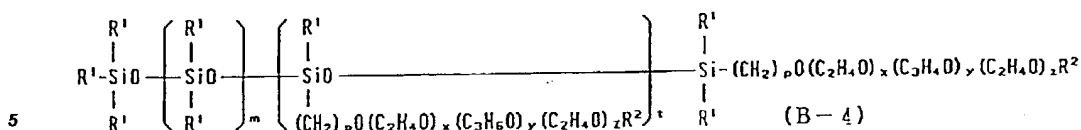
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1. A dye composition for keratinous fibers characterized by comprising the following ingredients (A), (B) and (C):

- (A) a direct dye,  
 (B) a polyoxyalkylene modified organopolysiloxane which contains 3 to 30% by weight of a polyoxyalkylene group in a molecule thereof, and is dispersible in water,  
 (C) an organic solvent,  
 5 and having a PH of 2.0 to 4.5.
2. A dye composition according to Claim 1, wherein the proportions of the ingredients (A), (B) and (C) are  
 (A) 0.01 to 5% by weight,  
 (B) 0.01 to 10% by weight and  
 10 (C) 0.5 to 50% by weight  
 based on the total weight of the composition.
3. A dye composition according to Claim 1, wherein the proportions of the ingredients (A), (B) and (C) are  
 (A) 0.02 to 0.1% by weight,  
 (B) 0.1 to 4% by weight,  
 15 (C) 1 to 35% by weight  
 based on the total weight of the composition.
4. A dye composition according to any of the preceding claims, wherein the direct dye (A) is an acid dye.
- 20 5. A dye composition according to any of claims 1 to 3, wherein the direct dye (A) is selected from the group consisting of C.I. Acid Yellow 23, C.I. Solvent Green 7, C.I. Acid Red 27, C.I. Acid Red 18, C.I. Food Green 3, C.I. Food Blue 2, C.I. Acid Blue 9, C.I. Acid Yellow 1, C.I. Acid Red 52, C.I. Pigment Red 57-1, C.I. Acid Orange 7, C.I. Acid Black 1, C.I. Acid Green 25 and Acid Violet 43.
- 25 6. A dye composition according to any of the preceding claims, wherein the polyoxyalkylene amodified organopolysiloxane (B) is selected from the group consisting of (B-1), (B-2), (B-3) and (B-4):

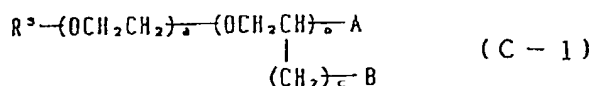


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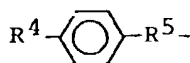


wherein R<sup>1</sup> is a C1 to C3 alkyl or phenyl group, R<sup>2</sup> is a hydrogen atom or a C1 to C12 alkyl group, m is an integer of 20 to 200, n is an integer of 1 to 10, x is an integer of 0 to 15, y is an integer of 0 to 10, z is an integer of 0 to 15, p is an integer of 1 to 5, t is an integer of 0 to 10, provided the sum of x+y+z is 1 or more but 20 or less.

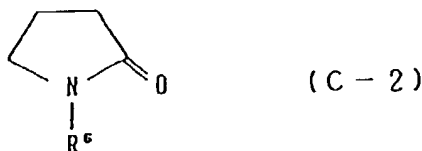
7. A dye composition according to any of the preceding claims, wherein the organic solvent (C) is selected from the group consisting of the compounds represented by formula (C-1), N-alkylpyrrolidones represented by formula (C-2), and C1 to C4 alkylene carbonates:



wherein R<sup>3</sup> is a hydrogen atom, a lower alkyl group or a group



wherein R<sup>4</sup> is a hydrogen atom, methyl group or a methoxy group, R<sup>5</sup> is a bond for bonding or a C1 - C3 saturated or unsaturated divalent hydrocarbon, A and B independently represent a hydrogen atom or a hydroxyl group, a, b and c independently represent an integer of 0 to 5, excepting the two cases where a=b=c=0 and A=H, and a=b=c=0, R<sup>3</sup>=H and A=OH;



wherein R<sup>6</sup> is a C1 - C18 linear or branched alkyl group.

8. A dye composition according to any of claims 1 to 6, wherein the organic solvent (C) is selected from the group consisting of ethanol, isopropanol, n-propanol, n-butanol, isobutanol, ethylene glycol, propylene glycol, isoprene glycol, 1,3-butanediol, benzyl alcohol, cinnamic alcohol, phenethyl alcohol, p-anisyl alcohol, p-methylbenzyl-alcohol, phenoxyethanol, 2-benzyloxy ethanol, methyl carbitol, ethyl carbitol, propyl carbitol, butyl carbitol, triethylene glycol monoethylether, triethylene glycol monobutyl ether, glycerol, N-methylpyrrolidone, N-octylpyrrolidone and N-laurylpyrrolidone,
9. A dye composition according to any of the preceding claims, wherein the pH falls in the range of from 2.5 to 4.5.
10. A dye composition according to any of the preceding claims, wherein the buffer index of an aqueous 10% solution of said dye composition is 0.01 to 0.2 gram equivalent/litre.
11. A dye composition according to any of the preceding claims, which is directly applied to the hair with bare hands or fingers, allowed to stand for 30 to 300 seconds and is subsequently rinsed off with water.
12. A method of dyeing the hair characterized by applying a composition comprising the following ingredients (A), (B) and (C),  
(A) a direct dye,

(B) a polyoxyalkylene modified organopolysiloxane which contains 3 to 30% by weight of a polyoxyalkylene group in a molecule thereof, and is dispersible in water,

(C) an organic solvent,

and having a pH of 2.0 to 4.5, directly to the hair with bare hands or fingers, allowing to stand for 30 to 300 seconds and then rinsing off with water.

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European Patent  
Office

# EUROPEAN SEARCH REPORT

Application Number

EP 92 31 0788

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
Y	EP-A-0 429 855 (KAO CORPORATION) * page 9; example 2 *	1-12	A61K7/13 A61K7/06
D,Y	GB-A-2 173 515 (BEECHAM GROUP PLC) * the whole document *	1-12	
Y	PARFUMS COSMÉTIQUES ARÔMES vol. 51, July 1983, PARIS (FRANCE) pages 67 - 72 DR. KOLLMEIER 'les copolymères polysiloxanes polyéthers comme additifs dans les formulations cosmétiques' * the whole document *	1-12	
D,A	DATABASE WPIL Week 8652, Derwent Publications Ltd., London, GB; AN 83-03088K & JP-A-57 192 310 (KAO CORPORATION) 26 November 1982 * abstract *	1-12	
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			A61K
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 15 MARCH 1993	Examiner SIERRA GONZALEZ
<p><b>CATEGORY OF CITED DOCUMENTS</b></p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons</p> <p>A : member of the same patent family, corresponding document</p>			

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